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Ingrid Wysong et al., "Comment on: An intermolecular potential for nitrogen from a multi-property analysis"

Journal article

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Comment on: An intermolecular potential for
nitrogen from a multi-property analysis

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February 23, 1999

1 Definitions and Correction

A recent paper by Cappelletti *et al.*[1] (CVPHD) makes use of classical trajectory (CT) effective kinetic cross sections on an optimized potential energy surface to predict Z for nitrogen gas over a range of temperatures. It is suggested here that an alternative method of conversion between the calculated cross sections and the rotational relaxation quantities (η_v , the volume viscosity, and Z , the rotational collision number) may give more physically meaningful results.

First, a clarification regarding a typographical error in eq. (3) of CVPHD. Z is defined as: τ_{rot}/τ_c where τ_{rot} is the rotational relaxation time and τ_c is the collision time.

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$$\tau_{\text{rot}} = \frac{\eta_v}{q^2 p} \sim \frac{kT q^2}{p \bar{v} \mathfrak{S}(0001)}, \quad (1)$$

where q^2 is defined as $k c_{\text{int}} / c_v^2$, k is Boltzmann's constant, p is the pressure, T is the temperature, \bar{v} is the average thermal velocity, and $\mathfrak{S}(0001)$ is the effective cross section for first-order internal energy relaxation, while $\mathfrak{S}(0010)$ is the cross-section for translational energy relaxation. The approximate result is true to first order where we have used:

$$\eta_v^{(1)} = \frac{2c_{\text{int}}^2 k T}{3c_v^2 \bar{v} \mathfrak{S}(0010)} = \frac{q^2 k T}{\bar{v} \mathfrak{S}(0001)}, \quad (2)$$

$$\mathfrak{S}(0010) = \frac{2c_{\text{int}}}{3k} \mathfrak{S}(0001). \quad (3)$$

The superscript (1) indicates a first order result and the superscript (2), used below, a second-order result. We use: c_p is the isobaric ideal gas heat capacity, c_v is the isochoric heat capacity, and c_{int} is the internal isochoric heat capacity

$$\tau_c = \frac{\pi \eta}{4p} \sim \frac{k T \pi}{4p \bar{v} \mathfrak{S}(2000)}, \quad (4)$$

where η is the shear viscosity. In the case of shear viscosity, higher-order corrections are quite small. Combining expressions leads to:

$$Z = \frac{4\eta_v}{\pi \eta q^2} \sim \frac{4\mathfrak{S}(2000)}{\pi \mathfrak{S}(0001)}. \quad (5)$$

This expression, not equation (3) of CVPHD, reproduces the first order Z curve of figure (6) in CVPHD. The curve in that figure which is labelled second-order Z cannot be consistently reproduced.

The expression for second-order volume viscosity, which will be used below is:

$$\eta_v^{(2)} = \frac{2c_{\text{int}}^2 k T S_{11}^0}{3c_v^2 \bar{v} S^0}, \quad (6)$$

where S^0 (as defined by Heck *et al.* [2]) is the determinant of a matrix of sixteen effective cross-sections, but is most strongly influenced by $\mathfrak{S}(0010)$, and S_{11}^0 is the determinant of the minor.

2 Comment

The point of this comment is to raise the question of the most appropriate value of c_{int} to use in the above expressions. Table 1 shows the values for c_p , the isobaric ideal gas heat capacity, and the implied values for c_v , the isochoric heat capacity, and c_{int} , the internal isochoric heat capacity, as well as the values for shear viscosity, recommended by Millat and Wakeham [3] for several temperatures. It has been assumed by CVPHD that the values for c_{int} due to Millat and Wakeham should be used in the above expressions. If this is done, then the identity eq. 3 does not hold true, and one may obtain two different results for η_v and Z by using the CT result for $\mathfrak{S}(0010)$ or by using the CT result for $\mathfrak{S}(0001)$ and eq. 3 to calculate $\mathfrak{S}(0010)$. Row A of the table shows the results when $\mathfrak{S}(0001)$ is used with eq. 3 to obtain a value for $\mathfrak{S}(0010)$ which is then put into eqs. 2 through 6 to obtain η_v and Z in first and second order. Row B shows the result when $\mathfrak{S}(0010)$ is used directly in eqs. 2 through 6.

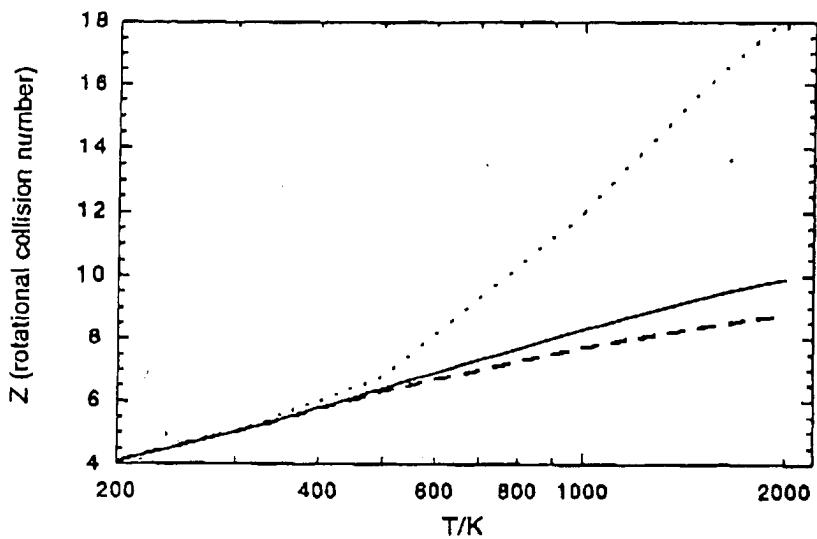
However, for temperatures above 300 K, the measured value of c_{int} begins to reflect an appreciable contribution from the vibrational mode of the nitrogen molecule. This contribution is, of course, not accounted for in the calculated cross sections, which assume a rigid-rotor molecule. Therefore, it is inconsistent to combine a $c_{int} = c_{rot} + c_{vib}$ value in equations with cross sections that are for rotation only. It is preferable to use $c_{int} = 1$ in the above expressions, which is the value that theoretically would be observed (above 300 K) if the vibrational mode were rendered completely inactive, to be consistent with the rigid-rotor assumption of the CT calculations.

Of course, if one does this, one should be careful not to compare the value obtained for volume viscosity with any measured value that includes a significant contribution from the vibrational mode. Comparisons should still be valid with any measured quantities, or model predictions, that include only contributions from rotational relaxation. This would include predicted values for Z based on state-to-state rotational energy transfer models [4]; or measured values for

volume viscosity if the rotational relaxation time is so much shorter than the vibrational relaxation time that it can be measured as a separate quantity. Such comparisons would still require the assumption that the rotational mode is completely decoupled from the vibrational mode. Note that Carnvale *et al.* [5] specifically assume that vibration is frozen in their analysis of nitrogen acoustic absorption data, even up to their maximum temperature of 1300 K.

The results obtained when the value $c_{int} = c_{rot} = k$ and $c_v = 2.5k$ are used in the above expressions are shown in row C of the table. In this case, no additional column is needed to show the results based on $\mathfrak{S}(0001)$ or $\mathfrak{S}(0010)$, since for $c_{int} = k$ the identity equation (3) holds true and both cross-sections yield the same values of η_v and Z . $c_v = 2.5k$ is the value that would hypothetically be observed if vibration were rendered completely inactive, which is the assumption most consistent with the rest of the present argument. Note that the results in row A are rather fortuitously close to those in row C. This is because the use of the measured value for c_{int} increases the term c_{int}^2/c_v^2 in equation (2), but the measured value for c_{int} then produces an offsetting decrease due to a larger value of $\mathfrak{S}(0010)$ based on the relation in equation (3).

Figure 1. Second-order results for Z using the three methods of calculation: Case A, $\mathfrak{S}(0001)_{CT}$; Case B, $\mathfrak{S}(0010)_{CT}$; Case C, $c_{int} \equiv k$



The three different results for Z (second-order) for the temperatures discussed here are shown in figure 1. The result for row B can be seen to turn up sharply at higher temperatures. This behaviour would appear to be inconsistent with the best information currently available on Z for nitrogen from a variety of sources [6]. In addition, the use of the measured value of c_{int} creates the difficulty of arbitrarily choosing one of the two calculated cross-sections which produce conflicting values of Z . These observations support the consistency argument put forward above for using $c_{int} = c_{rot} = k$ in this context. In addition, the need to move toward a method of calculating transport cross-sections that is not limited to the rigid rotor model is underlined.

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- [2] HECK, E. L., DICKINSON, A. S., and VESOVIC, V., 1994, *Molec. Phys.*, **83**, 907.

temperature		300 K	500 K	1000 K	1500 K	2000 K
measured	c_p/k	3.507	3.560	3.934	4.192	4.328
heat capacity	c_v/k	2.507	2.560	2.934	3.192	3.328
shear viscosity	c_{int}/k	1.007	1.060	1.434	1.692	1.828
Case A	$\eta_v^{(1)}$	9.7	17.5	35.9	51.4	65.7
	$\eta_v^{(2)}$	11.3	20.9	41.9	59.0	74.8
$\mathfrak{S}(0010) \equiv$	$Z^{(1)}$	4.3	5.3	6.7	7.3	7.7
$2c_{rot}/k\mathfrak{S}(0001)_{CT}$	$Z^{(2)}$	5.0	6.3	7.8	8.4	8.8
Case B	$\eta_v^{(1)}$	9.8	18.5	51.4	87.0	120.2
	$\eta_v^{(2)}$	11.4	22.4	64.6	111.1	155.1
$\mathfrak{S}(0010) \equiv$	$Z^{(1)}$	4.4	5.6	9.5	12.4	14.1
$\mathfrak{S}(0010)_{CT}$	$Z^{(2)}$	5.0	6.8	12.0	15.8	18.2
Case C	$\eta_v^{(1)}$	9.8	17.4	34.3	49.5	63.8
	$\eta_v^{(2)}$	11.3	20.9	43.2	63.3	82.3
$c_{int} \equiv 1$	$Z^{(1)}$	4.4	5.3	6.6	7.3	7.7
$c_v \equiv 2.5$	$Z^{(2)}$	5.0	6.4	8.3	9.3	9.9

Table 1: Calculated values for η_v and Z using CT cross sections. Values for η and η_v are in units of $10^{-5} g/(cmsec)$.

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